Graphitization of CVD Diamond Thin Film by X-Ray Synchrotron Radiation

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INTRODUCTION

CVD diamond films are attracting widespread interest due to their potential applications ranging from wear resistant coatings and thermal spreaders to optical and micro-electronic parts. The quality of the diamond films has recently been improved significantly by increasing the plasma density of the CVD deposition region, and nearly flat, polycrystalline diamond films with well aligned (100) surfaces can be obtained by bias-enhanced nucleation treatment and a controlled growth process [1-4]. It is, however, still very difficult to define the diamond quality quantitatively and to understand the various impurity distributions in the polycrystalline CVD diamond precisely. Raman spectroscopy has been the most popular analysis method to know the impurity of graphite and amorphous carbon relatively to diamond but it has some limitations to determine the quantitative amount clearly. Polycrystalline CVD diamond films have many defects like twins, vacancies, inclusions, grain boundaries, and surface imperfections, and in these defect areas some structural defects of graphite and/or amorphous carbon can easily be included. The near edge x-ray absorption fine structure (NEXAFS) analysis of the C K-edge is a very useful method to differentiate the carbon bonds (sp^1, sp^2, and sp^3) more exactly. For the understanding of CVD diamond films, several NEXAFS studies were performed and the basic differece from graphite and amorphous carbon were determined[5-8], but quantitative analysis of the graphite component in diamond has not seen yet.

During the NEXAFS study of various grades of CVD diamond films, we observed the change of peak shape and height. This change showed clearly the graphitization of the diamond films by x-ray synchrotron radiation damage. To study this phenomena more clearly, we increased radiation time and radiation intensity and observed the structure variation.

EXPERIMENTAL

Diamond films were synthesized on a silicon wafer by microwave plasma CVD process. During the deposition, 4000W power was applied and the substrate temperature was kept at 950°C. Gas pressure and composition was 110 Torr and 6% methane and 94% hydrogen, respectively. Deposition was performed for 15 minutes and the diamond film thickness was 0.67μm.

NEXAFS measurements were done at the photo-emission electron microscope situated at the undulator beamline 8.0 of the ALS. Exposure time was accumulated by repeated NEXAFS measurement. After five repeated measurement, the entrance and exit slit of the beamline were completely opened and maximum radiation was applied for 10 minutes before the sixth and seventh measurement, respectively. The mean photon number per second was calculated by averaging the integration of the I_0 current data, and the total photon number was calculated by accumulating the applied radiation time.

RESULTS and DISCUSSION

The diamond film synthesized in the microwave plasma CVD process showed gray color but the very good quality of diamond was obtained, as shown in the Raman spectrum in Fig.1, even though the high methane gas composition was applied. The sharp peak at a wave number of 1332cm^{-1} has very narrow full width at half maximum, which means that the diamond quality is very good. Also, a broad and very low peak around the wave number of 1550 cm^{-1} exhibits that a very small amount of graphite and/or amorphous carbon exists in the diamond film.

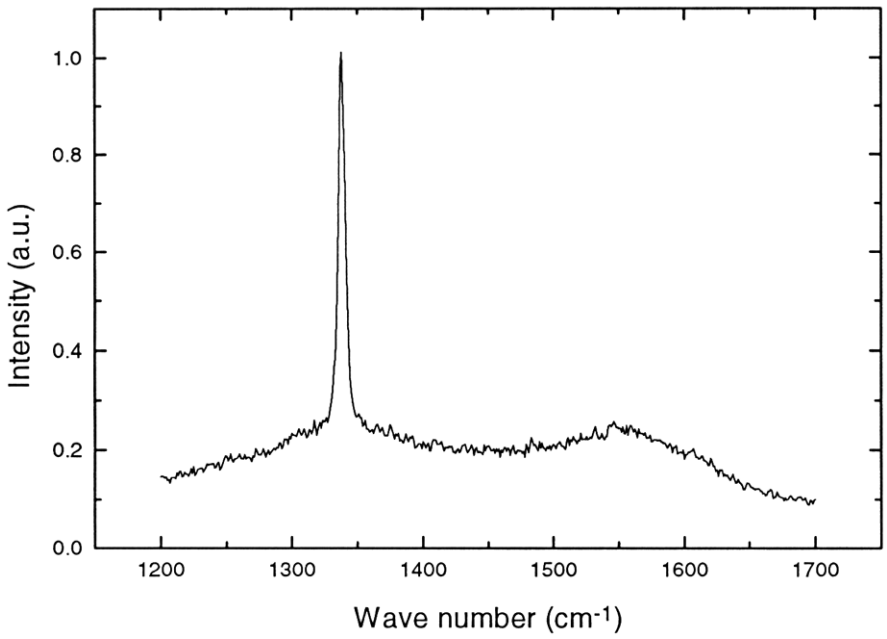

Fig.1. Raman spectrum of CVD diamond film synthesized at 950°C and with 6% methane gas composition at a pressure of 110 Torr.

NEXAFS measurements were performed by repeated energy scans. The measured NEXAFS plots are summarized in Fig.2. The number written on each curve indicates the total number of accumulated photons radiated on the film sample. All carbon K-edge spectra showed similar peaks in the range between 285 eV to 315 eV but the peak height varied. The first spectrum of original film showed a typical diamond spectrum except for a small amount of sp^2 component. This is consistent with the Raman spectra of Fig.1. As the radiation on the film increased, the sp^2 peak at 285 eV increased and the typical diamond peak between 289 eV and 310 eV decreased gradually. Even after the severe radiation of 18×10^{17} photon, the typical diamond peaks including the exciton peak at 289 eV remained visible. When the radiated surface was investigated by optical microscope after NEXAFS measurements, a circle with about 200 μm diameter with a black core circle of 10 μm diameter was seen. The outer circle is consistent with the beam size and the inner circle seemed to be the area where the transformation from diamond to graphite occurred on the film surface. More analysis is needed to identify the radiated and graphitized surface but the surface of the diamond film in the irradiated center part clearly showed a transformation from diamond to graphite.

It is clear here that the diamond surface is very sensitive to radiation damage and that the structure analysis should be performed below a certain threshold number of photons. Graphitization of roughened diamond is reported to be possible at temperatures of more than 1500°C [9].

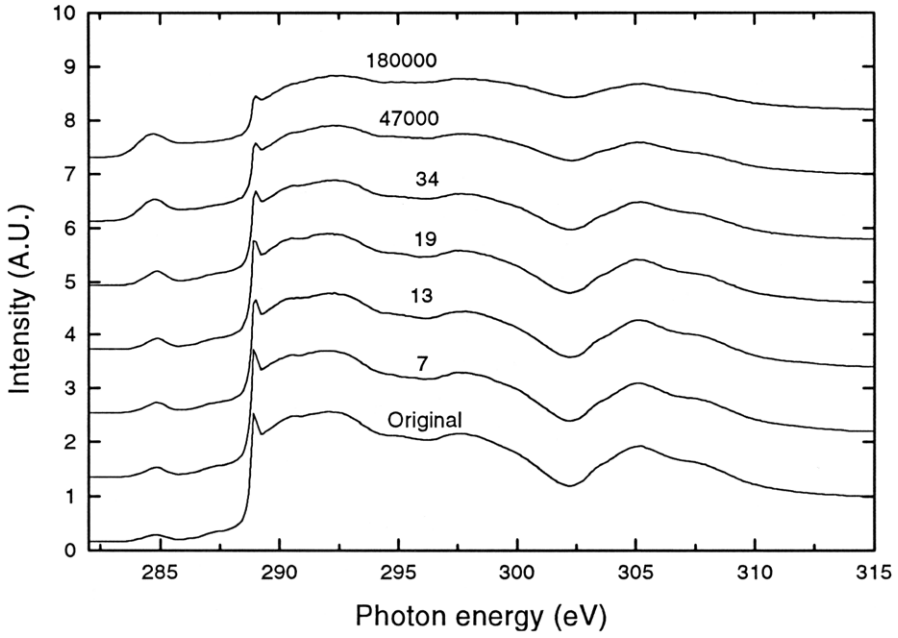

Fig.2. Carbon K-edge NEXAFS spectra for the diamond film which received x-ray synchrotron radiation repeatedly. The number on the curve is the accumulated number of irradiated photons which should be multiplied by 10^{13}.

CONCLUSION

Diamond thin films were synthesized by microwave plasma CVD and carbon K-edge NEXAFS measurement were performed. During NEXAFS measurements, radiation damage was observed and a graphitization of the diamond film surface was detected. For quality analysis of diamond films by measuring the sp^2 component, x-ray synchrotron radiation exposure should be limited by a threshold number of photons, which should be determined for each individual case.

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